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An Approximate Theory of Interfacial Tensions of Multicomponent Systems: Applications to Binary Liquid-Vapor Tensions

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Formulas obtained by approximation of the rigorous expression for the interfacial tension of multicomponent, polyatomic fluids are shown to provide accurate and simple estimates of the composition dependence of the surface tension of nonaqueous, binary solutions at low vapor pressures. Similar formulas are recommended for multicomponent (that is, more than two components) solutions.

SCOPE

From the Fowler model (1937) [also known as the Fowler-Kirkwood-Buff (1949) model], an expression is obtained relating interfacial tension of multicomponent systems to quantities dependent on intermolecular pair

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potential and pair correlation functions. As a special case, a simple formula is obtained, relating surface tension to composition at low vapor pressures. This formula, like Eberhart's (1966) and others, involves a parameter that is difficult to determine theoretically, since pair potential and correlation functions are not generally available. This parameter was determined by a simplified model and by fitting experimental data.

CONCLUSIONS AND SIGNIFICANCE

For many systems, the parameter is approximately unity, in fairly good agreement with an estimate given by Girifalco and Good (1957) for the parameter, making it possible to predict the composition dependence of surface tension from pure component data quite accurately. This also suggests a basis for defining ideal surface

tension, being that tension predicted by a value of unity for the parameter, and excess surface tension, the deviation from the ideal surface tension. Our model works well for nonaqueous systems but not for aqueous ones. If the parameter is obtained by fitting a single piece of experimental data, the fit is improved.

THEORY

Consider a fluid of N molecules, N_α of species α , $\alpha = 1, \dots, \nu$, described by a Hamiltonian of the form

$$H = \sum_{i=1}^N \frac{p_i^2}{2m_i} + U_N(\{\mathbf{r}\}, \{I\}) + H^I \quad (1)$$

If U_N is assumed to be pairwise additive, then the interfacial tension of a planar interface may be computed from the expression (H. T. Davis, 1975)

$$\gamma = - \sum_{\alpha, \beta=1}^{\nu} \sum_{\substack{\mathbf{r}_\alpha, \mathbf{r}_\beta \\ I_\alpha, I_\beta}} \frac{1}{2} \int_{-\infty}^{\infty} dz_1 \int d^3r_{12} \left[z_{12} \frac{\partial u_{\alpha\beta}}{\partial z_{12}}(\mathbf{r}_{12}; I_\alpha, I_\beta) - x_{12} \frac{\partial u_{\alpha\beta}}{\partial x_{12}}(\mathbf{r}_{12}; I_\alpha, I_\beta) \right] \rho_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2, I_\alpha, I_\beta) \quad (2)$$

The normal to the interface is in the z direction.

At low vapor pressures, the Fowler approximation to $\rho_{ji}^{(2)}$ leads to a fairly good estimate of γ for the surface tension of simple, one-component fluids. The purpose of the present paper is to apply a version of the Fowler approximation to multicomponent, polyatomic fluids.

The basic assumption of the model is that $\rho_{\alpha\beta}^{(2)}$ may be approximated by the expression

$$\rho_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2, I_\alpha, I_\beta) = n_\alpha(z_1) n_\beta(z_2) g_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, I_\alpha, I_\beta) \quad (3)$$

where

$$\begin{aligned} n_\alpha(z_i) &= n_\alpha^{(1)}, & z_i < 0 \\ &= n_\alpha^{(2)}, & z_i > 0 \end{aligned} \quad (4)$$

The pair correlation function $g_{\alpha\beta}$ is assumed to obey the expression

$$\begin{aligned} g_{\alpha\beta} &= g_{\alpha\beta}^{(1)}, & z_1, z_2 < 0 \\ &= g_{\alpha\beta}^{(1,2)}, & z_1 < 0, z_2 > 0 \\ &= g_{\alpha\beta}^{(2,1)}, & z_1 > 0, z_2 < 0 \\ &= g_{\alpha\beta}^{(2)}, & z_1, z_2 > 0 \end{aligned} \quad (5)$$

$g_{\alpha\beta}^{(i)}$ is the pair correlation function of species α and β in bulk phase i and $g_{\alpha\beta}^{(i,j)}$ is the correlation function of species α and β interacting across the phase boundary

at $z = 0$. Such cross terms did not enter Fowler's formula, since he assumed the vapor density to be zero.

Using Equations (3) to (5) in Equation (2) and performing manipulations similar to those given by H. T. Davis (1975), we obtain the expression

$$\begin{aligned} \gamma &= \sum_{\alpha, \beta=1}^{\nu} [n_\alpha^{(1)} n_\beta^{(1)} B_{\alpha\beta}^{(1)} + n_\alpha^{(2)} n_\beta^{(2)} B_{\alpha\beta}^{(2)} \\ &\quad - n_\alpha^{(1)} n_\beta^{(2)} B_{\alpha\beta}^{(1,2)} - n_\alpha^{(2)} n_\beta^{(1)} B_{\alpha\beta}^{(2,1)}] \quad (6) \end{aligned}$$

where

$$B_{\alpha\beta}^{(i)} \equiv \frac{1}{2} \sum_{I_\alpha, I_\beta} \int_{z_{12} > 0} d^3r_{12} z_{12} \left[z_{12} \frac{\partial u_{\alpha\beta}}{\partial z_{12}} - x_{12} \frac{\partial u_{\alpha\beta}}{\partial x_{12}} \right] g_{\alpha\beta}^{(i)} \quad (7)$$

and $B_{\alpha\beta}^{(i,j)}$ has the same form as $B_{\alpha\beta}^{(i)}$ except that $g_{\alpha\beta}^{(i,j)}$ appears in place of $g_{\alpha\beta}^{(i)}$. For particles interacting with pairwise additive, centrally symmetric forces, Equation (7) reduces to the form

$$B_{\alpha\beta}^{(i)} = \frac{\pi}{8} \int_0^\infty dr r^4 \frac{du_{\alpha\beta}(r)}{dr} g_{\alpha\beta}^{(i)}(r) \quad (8)$$

where $g_{\alpha\beta}^{(i)}(r)$ is the radial distribution function [defined as $\sum_{I_\alpha, I_\beta} g_{\alpha\beta}(r, I_\alpha, I_\beta)$]. Equation (8) was obtained by Kirkwood and Buff (1949) for a one-component fluid.

In the special case of a low vapor pressure liquid-vapor interface, say phase 1 is liquid, $n_\alpha^{(2)} \ll n_\alpha^{(1)}$, so that Equation (6) reduces to

$$\gamma \simeq \sum_{\alpha, \beta=1}^{\nu} n_\alpha^{(1)} n_\beta^{(1)} B_{\alpha\beta}^{(1)} \quad (9)$$

This is the multicomponent version of the Fowler model.

Another special case is a two-component, two phase system in which component 1 is almost immiscible in Phase 1 and component 2 is almost immiscible in Phase 2. Equation (6) in this instance becomes

$$\gamma \simeq [n_1^{(1)}]^2 B_{11}^{(1)} + [n_2^{(2)}]^2 B_{22}^{(2)} - 2n_1^{(1)} n_2^{(2)} B_{12}^{(1,2)} \quad (10)$$

This result is equivalent to the expression introduced by Girifalco and Good (1957) and by B. W. Davis (1975) to relate the interfacial tension of an immiscible liquid pair to the surface tensions of pure liquids. A formula like Equation (10) with equal B_{ij} 's was presented by Green (1960) for a simple liquid in equilibrium with its vapor.

ESTIMATION OF SURFACE TENSIONS OF BINARY SOLUTIONS

Although molecular dynamics and perturbation theory have finally begun to produce molecular structural information for polyatomic fluids, for the most part, the pair potentials and the pair correlation functions of polyatomic fluids are not well characterized enough to compute the $B_{\alpha\beta}$ quantities needed to predict interfacial tensions from Equation (6). We shall demonstrate here, however, that the model furnishes a useful semiempirical method for estimating the composition dependence of the surface tension of binary solutions.

Let us assume that the composition dependence of the coefficients $B_{\alpha\beta}$ can be neglected and define the mixing parameter Φ :

$$\Phi = B_{\alpha\beta} / \sqrt{B_{\alpha\alpha}B_{\beta\beta}} \quad (11)$$

Under this assumption, the form of Equation (9) for a binary solution becomes

$$\gamma = \left(\frac{n_1}{n_1^0}\right)^2 \gamma_1^0 + \left(\frac{n_2}{n_2^0}\right)^2 \gamma_2^0 + 2\Phi \frac{n_1 n_2}{n_1^0 n_2^0} (\gamma_1^0 \gamma_2^0)^{1/2} \quad (12)$$

where γ_α^0 and n_α^0 denote, respectively, the surface tension and saturated liquid density of pure α at the same temperature as the solution, n_α denotes the density of component α in the liquid solution. If the vapor density is not negligible compared to the liquid density, the expression corresponding to Equation (12) is

$$\gamma = \left(\frac{n_{1,l} - n_{1,v}}{n_{1,l}^0 - n_{1,v}^0}\right)^2 \gamma_1^0 + \left(\frac{n_{2,l} - n_{2,v}}{n_{2,l}^0 - n_{2,v}^0}\right)^2 \gamma_2^0 + 2\Phi \left[\left(\frac{n_{1,l} - n_{1,v}}{n_{1,l}^0 - n_{1,v}^0}\right) \left(\frac{n_{2,l} - n_{2,v}}{n_{2,l}^0 - n_{2,v}^0}\right) \right] (\gamma_1^0 \gamma_2^0)^{1/2} \quad (13)$$

$n_{\alpha,l}$ and $n_{\alpha,v}$ denote liquid and vapor densities of component α . For the computations reported herein, $n_{\alpha,v} \ll$

TABLE I

System	$T, ^\circ\text{C}$	γ_1^0 $N\text{-}m \times 10^3$	γ_2^0 $N\text{-}m \times 10^3$	x_1	$\Phi(x_1)$	$\bar{\Delta}$	Δ_{\max}	Φ_{GG}	$\bar{\Delta}_{GG}$	$\Delta_{GG\max}$	$\bar{\Delta}_1$	$\Delta_{1\max}$
Ethanol-water ^a	30	20.76	71.03	0.5303	0.6	0.19	0.43	0.96	0.31	0.62	0.32	0.64
Methanol-water ^b	30	21.04	71.03	0.4577	0.68	0.06	0.14	0.98	0.17	0.27	0.18	0.28
Isooctane-cyclohexane ^c	30	17.89	23.77	0.4838	0.97	0.00	0.01	1.00	0.02	0.02	0.02	0.02
Isooctane-benzene ^d	30	17.89	27.53	0.4829	0.92	0.00	0.01	0.99	0.03	0.04	0.03	0.04
Isooctane-dodecane ^e	30	17.89	24.47	0.5172	0.98	0.00	0.01	1.00	0.01	0.01	0.01	0.01
Chlorobenzene-toluene ^f	20	30.39	25.15	0.5095	0.94	0.00	0.02	1.00	0.02	0.04	0.02	0.04
Bromobenzene-toluene ^g	20	32.26	25.15	0.5025	1.02	0.01	0.02	1.00	0.01	0.02	0.01	0.03
Ethylene-dichloride-benzene ^h	17	31.68	29.17	0.5254	0.97	0.00	0.00	1.00	0.01	0.02	0.01	0.02
Dodecane-hexane ⁱ	30	24.31	17.43	0.3859	1.00	0.00	0.01	1.00	0.00	0.01	0.00	0.01
Ethanol-benzene ^j	25	25.15	27.26	0.3339	0.94	0.01	0.02	0.98	0.01	0.02	0.01	0.02
Methanol-benzene ^k	30	21.09	26.63	0.4496	0.94	0.01	0.02	0.98	0.01	0.02	0.01	0.02
Ethanol-phenol ^l	35	20.34	38.03	0.7208	1.02	0.02	0.06	1.00	0.01	0.05	0.01	0.05
Decanol-butanol ^m	25	28.30	24.18	0.5079	1.13	0.01	0.01	0.99	0.03	0.06	0.03	0.06
Methanol-decanol ⁿ	25	22.10	28.30	0.4741	1.04	0.01	0.04	0.94	0.02	0.03	0.01	0.02
Methanol-butanol ^o	25	22.10	24.18	0.4717	0.99	0.00	0.00	0.98	0.00	0.02	0.00	0.01
Ethanol-decanol ^p	25	21.83	28.30	0.4778	0.98	0.01	0.02	0.96	0.01	0.02	0.01	0.01
Propanol-decanol ^q	25	23.33	28.30	0.5015	0.98	0.01	0.02	0.98	0.01	0.02	0.01	0.01
i-propanol-decanol ^r	25	20.78	28.30	0.5117	1.01	0.00	0.00	0.98	0.00	0.01	0.00	0.01
Hexanol-decanol ^s	25	25.83	28.30	0.5002	1.00	0.00	0.01	1.00	0.00	0.01	0.00	0.01
Methanol-sec-butanol ^t	25	22.10	23.00	0.5120	1.01	0.00	0.00	0.98	0.00	0.00	0.00	0.01
Methanol-i-butanol ^u	25	22.10	22.44	0.4749	1.01	0.00	0.00	0.98	0.01	0.01	0.00	0.00
Methanol-tert-butanol ^v	25	22.10	20.11	0.5025	0.98	0.01	0.02	0.98	0.01	0.02	0.01	0.01
Cyclohexane-toluene ^w	25	24.38	27.94	0.5050	1.06	0.00	0.00	1.00	0.02	0.04	0.02	0.04
Cyclohexane-trans-decalin ^x	25	24.38	29.97	0.4709	1.03	0.00	0.00	1.00	0.01	0.01	0.01	0.01
Cyclohexane-cis-decalin ^y	25	24.38	32.24	0.5105	1.03	0.00	0.00	1.00	0.01	0.02	0.01	0.02
Cyclohexane-benzene ^z	20	24.38	28.86	0.5063	1.05	0.01	0.02	1.00	0.01	0.03	0.01	0.03
Cyclohexane-tetra-chloroethylene ^{aa}	25	24.38	31.30	0.5139	1.06	0.00	0.01	1.00	0.02	0.03	0.02	0.03
Cyclopentane-toluene ^{bb}	25	21.85	27.94	0.5081	1.05	0.00	0.00	1.00	0.01	0.02	0.01	0.02
Cyclopentane-benzene ^{cc}	25	21.85	28.20	0.5042	1.07	0.00	0.01	1.00	0.02	0.03	0.02	0.03
Cyclopentane-tetrachloro-ethylene ^{dd}	25	21.85	31.30	0.4901	1.06	0.00	0.01	1.00	0.02	0.03	0.02	0.03
Cyclopentane-carbontetra-chloride ^{ee}	25	21.85	26.13	0.4976	1.01	0.00	0.00	1.00	0.00	0.00	0.00	0.00
Benzene-o-xylene ^{ff}	25	28.20	29.44	0.4975	1.01	0.00	0.00	1.00	0.01	0.01	0.01	0.01

Sources of Experimental Data

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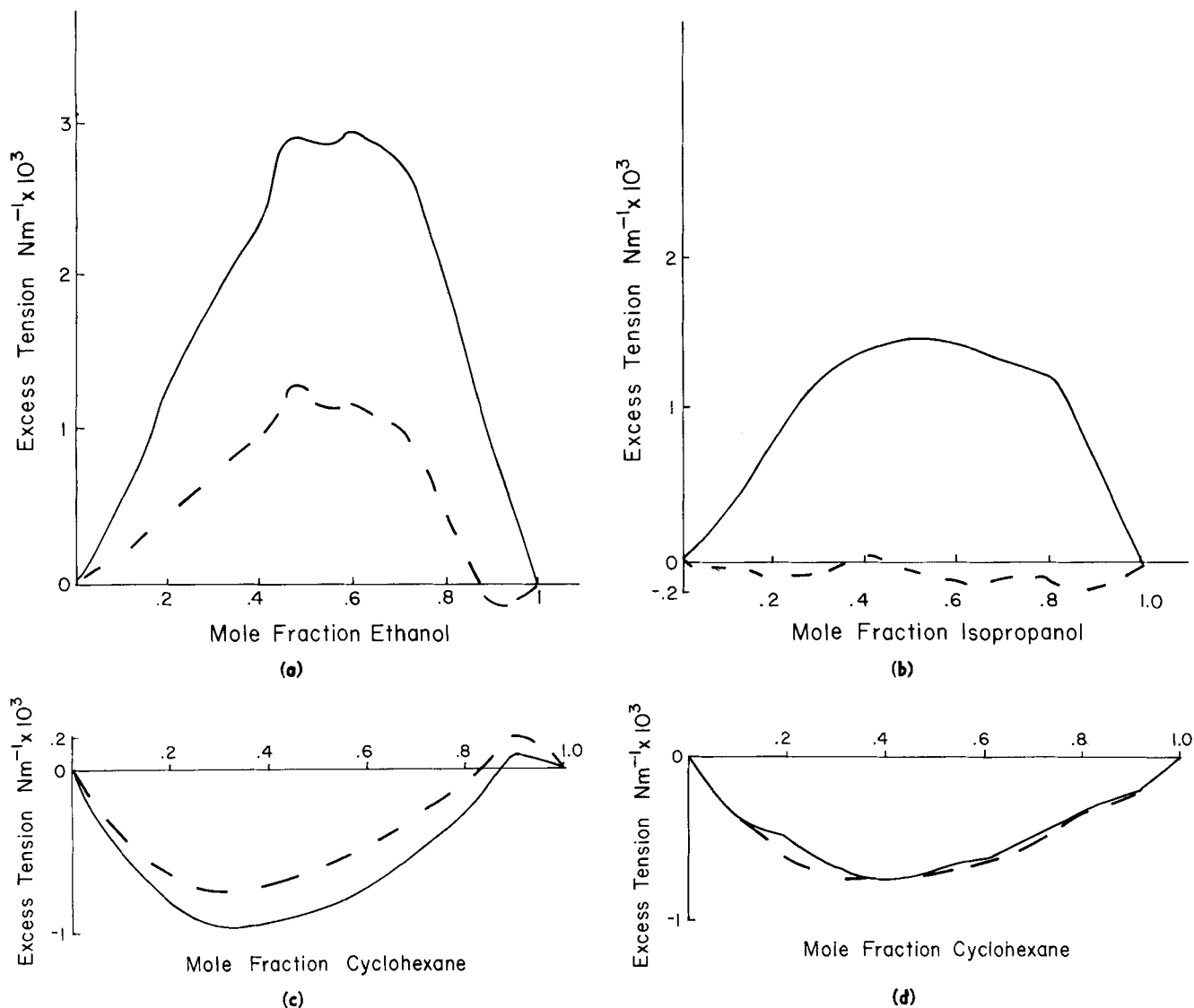


Fig. 1. Comparison of the excess tensions defined by $\gamma - \gamma_{\Phi=1}$ (dashed curves) with those defined by $\gamma - \sum x_i \gamma_i^0$ (solid curves). a. Ethanol-decanol. b. Isopropanol-decanol. c. Cyclohexane-benzene. d. Cyclohexane-tetrachloroethylene.

$n_{\alpha,b}$, so that Equation (12) is used instead of Equation (13).

The unknown parameter of the model is Φ . This is the same parameter that Girifalco and Good introduced in relating the interfacial tensions of immiscible liquids to the surface tensions of the pure liquids. For structureless fluids of particles interacting via pairwise additive, centrally symmetric forces, Girifalco and Good have given for Φ the following estimate:

$$\Phi_{GG} = \frac{4V_1^{1/3}V_2^{1/3}}{(V_1^{1/3} + V_2^{1/3})^2} \quad (14)$$

Estimating the values of V_α by $1/n_\alpha^0$, we have computed the values of Φ_{GG} shown in Table 1. n_α^0 denotes the density of pure component α at the temperature shown in the table.

Estimating the density n of the liquid solution from Amagat's law, $1/n = x_1/n_1^0 + (1 - x_1)/n_2^0$, where x_1 is the mole fraction of component 1, we have used Equation (12) with experimental γ_α^0 's to compute surface tensions as a function of composition for a number of binary solutions. The absolute error Δ

$$\Delta = |\gamma_{\text{calc}} - \gamma_{\text{exp}}|/\gamma_{\text{exp}}$$

averaged over some six to fifteen compositions between $x_1 = 0$ and $x_1 = 1$ is reported in Table 1 along with

the maximum absolute error Δ_{max} observed for the compositions considered.

With Φ 's predicted from Girifalco and Good's formula, Equation (14), the average absolute error $\bar{\Delta}_{GG}$ is quite small for all the nonaqueous systems reported in Table 1. For these systems, the average error is less than 3% except for the decanol-butanol solution, where it is 3%. The maximum $\Delta_{GG \text{ max}}$ is 6% for the decanol-butanol system and less than 6% for the other nonaqueous systems.

Since the values of Φ_{GG} are within a few percent of unity, we examined the consequence of setting $\Phi = 1$ in Equation (12). As indicated in Table 1 by the average and maximum errors $\bar{\Delta}_1$ and $\Delta_{1,\text{max}}$ for this case, setting Φ equal to unity provides as good predictions of the composition dependence of the surface tension as does computing Φ from the Girifalco and Good formula. We denote by $\gamma_{\Phi=1}$ the value of γ predicted by Equation (12).

Figures 1a to d show plots of $(\gamma - \gamma_{\Phi=1})$ and $(\gamma - x_1\gamma_1^0 - x_2\gamma_2^0)$ vs. mole fraction. As stated by Eberhart, surface tension is not a linear function of mole fraction. Overall, $\gamma_{\Phi=1}$ is a better approximation of γ than $(x_1\gamma_1^0 + x_2\gamma_2^0)$. This suggests that the excess surface tension $\gamma^E = \gamma - x_1\gamma_1^0 - x_2\gamma_2^0$ could be redefined as $\gamma^E = \gamma - \gamma_{\Phi=1}$, $\gamma_{\Phi=1}$ being the ideal surface tension. The accuracy and the theoretical basis of $\gamma_{\Phi=1}$ make it a more desirable ideal surface tension than its predecessor.

The model does not perform well for aqueous solutions. The average and maximum errors reported in Table 1 are quite large for aqueous solutions of methanol and ethanol.

From the results of our studies of binary solutions, we make the following recommendation for multicomponent, nonaqueous solutions. If the vapor density is small compared to the liquid density, if an error of a few percent can be tolerated in the surface tension, and if the surface tensions of the pure liquids are known, then the surface tension of the solution may be estimated from

$$\gamma = \sum_{\alpha, \beta=1}^{\nu} \frac{n_{\alpha} n_{\beta}}{n_{\alpha}^0 n_{\beta}^0} \sqrt{\gamma_{\alpha}^0 \gamma_{\beta}^0} \quad (15)$$

with the density n of the solution estimated from

$$1/n = \sum_{\alpha=1}^{\nu} x_{\alpha}/n_{\alpha}^0 \quad (16)$$

x_{α} denotes the mole fraction of component α . Of course, the component density n_{α} is given by $x_{\alpha}n$. The pure fluid surface tensions γ_{α}^0 may be obtained from experiment, theory or corresponding state estimates.

We also investigated the possible improvement in the accuracy of Equation (14) by determination of Φ by fitting theory to experiment at some composition x_1 near the equimolar point. The values of Φ , the compositions x_1 at which the Φ 's were determined, and the average and maximum absolute errors $\bar{\Delta}$ and Δ_{\max} are given in Table 1. Again, the model, though improved, performs poorly for aqueous systems. For the nonaqueous systems, however, the average error is exceedingly small, being 1% or less for all but one case. Thus, where some binary solution data are available, we recommend, as an improved version of Equation (15), the expression

$$\gamma = \sum_{\alpha, \beta=1}^{\nu} \frac{n_{\alpha} n_{\beta}}{n_{\alpha}^0 n_{\beta}^0} \Phi_{\alpha\beta} \sqrt{\gamma_{\alpha}^0 \gamma_{\beta}^0} \quad (17)$$

where by convention if $\alpha = \beta$, $\Phi_{\alpha\beta} = 1$, and if $\alpha \neq \beta$, $\Phi_{\alpha\beta}$ is determined by fitting theory to experiment for binary solutions. Of course, the advantage of Equation (15) over Equation (17) is that the former requires no experimental data on solutions.

From the computations given in Table 1, it appears that the assumption that the parameters $B_{\alpha\beta}$ are composition independent is reasonably correct for nonaqueous systems but is inaccurate for aqueous solutions. We presume the difficulty with water is associated with the hydrogen bonding structure of water, but, at the level of analysis pursued herein, we can furnish no further insight into the matter.

A final conclusion that we can draw for the nonaqueous systems considered in this paper is that the detailed nature of the molecular interactions and correlation functions, which would appear from Equation (7) to affect strongly the values of $B_{\alpha\beta}$, largely cancels out of the ratio $B_{\alpha\beta}/\sqrt{B_{\alpha\alpha}B_{\beta\beta}}$. This conclusion follows from the fact that Φ is nearly unity for all the nonaqueous systems considered. The implication of the success of the Girifalco-Good formula for predicting Φ is that the average volume of a molecule is the most important factor contributing to the ratio.

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NOTATION

- $B_{\alpha\beta}^{(i,j)}$ = defined by Equation (7)
 $B_{\alpha\beta}^{(i)}$ = defined by Equation (7)
 $g_{\alpha\beta}^{(i,j)}$ = pair correlation function of species α and β interacting across phase boundary between phases i and j
 $g_{\alpha\beta}^{(i)}$ = pair correlation function of species α and β in bulk phase i
 H = Hamiltonian, defined by Equation (1)
 H^I = internal Hamiltonian of molecules at infinite separation from one another
 m_i = mass of i^{th} molecule
 n_1 and n_2 = density of species 1 and 2
 n_1^0 and n_2^0 = density of pure i
 $n_{\alpha}^{(i)}$, $n_{\alpha,i}$ = bulk density of α in phase i
 p_i = center of mass momentum of i^{th} molecule
 $U_N(\{\underline{r}\}, \{\underline{J}\})$ = intermolecular interaction potential of molecules with center of mass at $\{\underline{r}\}$ and having internal energy states $\{\underline{J}\}$
 $U_{\alpha\beta}$ = pair potential of species α and β
 V_{α} = molar volume of component α
 X_i = mole fraction of component i

Greek Letters

- γ = surface tension
 γ_i = surface tension of component i
 γ_i^0 = surface tension of pure component i
 γ^E = excess surface tension
 Δ = absolute error, Φ fitted
 Δ_1 = absolute error, $\Phi = 1$
 Δ_{GG} = absolute error, $\Phi = \Phi_{GG}$
 Φ = mixing parameter, defined by Equation (11)
 Φ_{GG} = Girifalco and Good parameter, defined by Equation (14)
 $\rho_{\alpha\beta}^{(2)}$ = pair number density of species α and β

Subscripts and Superscripts

- max = maximum
 calc = calculated
 exp = experimental
 - = average

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